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Simple quantum model for correlations in random one-dimensional Heisenberg antiferromagnets

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Using a simple quantum model we calculate static correlations for the random $S=\frac{1}{2}$ Heisenberg antiferromagnets. The correlations decay exponentially with distance. In addition the second moment of a two-spin correlation function was evaluated. No agreement with experiment could be obtained when we tried to extract the correlation time of this correlation function from its second moment.

Many recently obtained, experimental results on quinolinium$(TCNQ)_2$ (TCNQ is tetracyanoquinodimethane)[1,2] have stimulated interest in the understanding of the random-exchange Heisenberg antiferromagnetic chain (REHAC). The REHAC was first introduced by Bulaevskii *et al.*[3] The most popular probability distribution function $P(J)$ for the random exchange is $P(J) \propto J^{-\alpha}$ for $J \leq J_0$ and $\alpha < 1$. Approximate calculations using this $P(J)$ lead to thermodynamic properties which strongly reflect the singular character of the distribution.[3-5] These simple models seem to fit the low-temperature thermodynamic properties of quinolinium$(TCNQ)_2$ quite well.[1] Recently it was argued that the exchange cutoff J_0 should be ridiculously high to fit the higher-temperature region of the magnetic susceptibility of quinolinium$(TCNQ)_2$. A different $P(J)$ was suggested which was claimed to fit the experimental data with more reasonable parameters.[6] Rather than discuss the more sophisticated approaches including the renormalization-group treatments,[7] we would like to point out that, apart from the work of Theodorou and Cohen[4] who used a classical model, in none of these theories *correlations* were calculated. The understanding of correlations and the knowledge of the amount of short-range order in these random systems is a crucial step towards the ultimate goal of understanding the dynamics of the REHAC. The large body of unexplained experimental results on the dynamic properties (NMR and EPR) of quinolinium$(TCNQ)_2$ form a real challenge.[2]

We present in this paper a simple quantum-mechanical model for the static correlations in the REHAC. These correlations will be used to calculate the second moment of a dynamic two-spin correlation function. Our model, although admittedly coarse, retains the full symmetry of the Hamiltonian, that is translational and rotational symmetry. The model can be solved exactly for zero magnetic field. An approximate solution for nonzero magnetic field will be discussed. Our results allow for semiquantitative predictions of the influence of temperature and the influence of $P(J)$ on the correlations. Of course, the results can also be applied to the uniform chain, but they do not show some of the very subtle properties of the one-dimensional uniform model like large zero-point fluctuations. It is however clear that in the random models many of these subtleties will not survive configurational averaging. So we discuss the model with the explicit intention to apply it to the random chain. Now we will present the model.

The Hamiltonian of a REHAC reads

$$H = 2\sum_{i=1}^{N} J(i)\vec{S}_i \cdot \vec{S}_{i+1} - \frac{h}{2}\sum_{i=1}^{N} S_{i,z} - \frac{h}{2}\sum_{i=1}^{N} S_{i+1,z} \equiv \sum_{i=1}^{N} H_i \quad . \tag{1}$$

The symmetrized form of the Zeeman interaction will prove to be useful later on. It can be demonstrated[8] that the partition function Z can be written as

$$Z = \lim_{m\to\infty} Z_m \quad , \tag{2a}$$

in which

$$Z_m = \mathrm{Tr}(e^{-\beta H_1/m} e^{-\beta H_2/m} \cdots e^{-\beta H_N/m})^m \quad . \tag{2b}$$

This formula is the basis for the path-integral formulations of quantum-statistical mechanics. The simplest approximant to Z is Z_1. Z_1 can be calculated exactly if $h=0$ with the help of transfer-matrix techniques.[9] For the uniform chain Z_1 can be calculated exactly also for nonzero magnetic field. Inserting complete sets in the product representation of Z_1 one finds,

$$Z_1 = \sum_{\{\psi,\phi\}} \langle \phi_1\psi_2 | e^{-\beta H_1} \psi_1\phi_2\rangle \cdots \langle \phi_N\psi_1 | e^{-\beta H_N} \psi_N\phi_1\rangle \tag{3}$$

in which ϕ_i and ψ_i denote spin-wave functions (up or down) of the spin at site i. We will use the notation $-\phi_i$ to indicate the wave function having the spin component opposite to ϕ_i. It is straightforward to calculate the 4×4 matrix $\langle \phi_j\psi_{j+1}|e^{-\beta H_j}\psi_j\phi_{j+1}\rangle$.[8] The structure of this matrix is such that nonzero elements will only result either if both $\phi_j=\psi_j$ and $\phi_{j+1}=\psi_{j+1}$ or if both $\phi_j=-\psi_j$ and $\phi_{j+1}=-\psi_{j+1}$. This allows us to rewrite Z_1 as,

$$Z_1=\sum_{\{\psi\}}\prod_{i=1}^{N}T_i^+(\psi_i,\psi_{i+1})+\sum_{\{\psi\}}\prod_{i=1}^{N}T_i^-(\psi_i,\psi_{i+1}) \quad , \tag{4}$$

in which the two two-dimensional transfer matrices are defined by

$$T_i^{\pm}(\psi_i,\psi_{i+1})=\langle\psi_i\pm\psi_{i+1}|e^{-\beta H_i}\pm\psi_i\psi_{i+1}\rangle \quad .$$

The problem can now be treated with standard transfer-matrix theory.[9] The eigenvalues of $\underline{T}_i^+$ will be denoted by $\Lambda_{i,\pm}^+$ and the two degenerate eigenvalues of $\underline{T}_i^-$ will be denoted by Λ_i^-,

$$\Lambda_{i,\pm}^+=e^{1/2\beta J(i)}\{\cosh(\beta h/2)\pm[\sinh^2(\beta h/2)+\tfrac{1}{4}(1+e^{-2\beta J(i)})^2]^{1/2}\} \quad , \tag{5a}$$

and

$$\Lambda_i^-=\tfrac{1}{2}e^{1/2\beta J(i)}(1-e^{-2\beta J(i)}) \quad . \tag{5b}$$

The eigenfunctions will be denoted by $\Phi_{i,\pm}^+$ and $\Phi_{i,\pm}^-$, which in the case of zero magnetic field are given by

$$\Phi_{i,\pm}^+=\frac{1}{\sqrt{2}}\begin{pmatrix}1\\ \pm 1\end{pmatrix},\quad \Phi_{i,+}^-=\begin{pmatrix}1\\0\end{pmatrix},\quad\text{and }\Phi_{i,-}^-=\begin{pmatrix}0\\1\end{pmatrix} \quad .$$

In the case of nonzero magnetic field the eigenfunctions depend on $J(i)$ and for that reason they are not orthogonal in REHAC models. For the moment we will confine ourselves to zero magnetic field. In the thermodynamic limit only the largest eigenvalue of $\underline{T}^{\pm}$ will survive, so that for a specific configuration of exchange constants

$$\ln Z_1=\sum_{i=1}^{N}\Lambda_{i,+}^+ \quad , \tag{6a}$$

which after having done the configurational average over $P(J)$ results in

$$\langle\ln Z_1\rangle=N\int P(J_i)\Lambda_{i,+}^+dJ_i \quad . \tag{6b}$$

The integration over $P(J)$ can be done analytically for a simple $P(J)$ and in more complicated cases low-temperature expressions can be found analytically. It is now simple to calculate the energy and the specific heat by using $\langle E\rangle=-\partial\langle\ln Z_1\rangle/\partial\beta$ and $\langle C_v\rangle=-\beta^2\partial\langle E\rangle/\partial\beta$. To give actual results we have to specify $P(J)$. We will first discuss[4,5]

$$P(J)=\frac{1-\alpha}{J_0}\left(\frac{J}{J_0}\right)^{-\alpha} \quad , \tag{7}$$

for $0\le J\le J_0$ and $\alpha\simeq 0.8$. The low-temperature results ($\beta J_0\gg 1$) agree exactly, apart by a trivial factor of 2, with the results of the exchange-coupled pair model of Clarke and Tippie (CT),[5] showing that their results can be obtained without destroying the symmetry of the REHAC. The magnetic susceptibility will be calculated using the fluctuation-dissipation theorem, which expresses the susceptibility in terms of two-spin correlation functions.

The two-spin correlations can be calculated with the same transfer-matrix technique. The result in zero magnetic field reads

$$\langle S_{i,x}S_{i+j,x}\rangle=\frac{1}{4}\left[\int P(J_i)\left(\frac{\Lambda_{i,-}^+}{\Lambda_{i,+}^+}\right)dJ_i\right]^{|j|} \quad , \tag{8}$$

the same expression holding for the z correlations. The low-temperature result using Eq. (7) is given by

$$\langle S_{i,x}S_{i+j,x}\rangle=\tfrac{1}{4}[-1+2^{1+\alpha}(\beta J_0)^{\alpha-1}f_1(\alpha)]^{|j|} \quad , \tag{9}$$

in which $f_1(\alpha)$ is a function introduced by CT, and $f_1(\alpha\simeq 0.8)\simeq 0.25$. Using the fluctuation-dissipation-theorem result $\chi/\chi_f=\frac{4}{3}\sum\langle\vec{S}_i\cdot\vec{S}_{i+j}\rangle$, where χ_f is the free-spin susceptibility, one finds to leading order in βJ_0,

$$\frac{\chi}{\chi_f}=2^{1+\alpha}(\beta J_0)^{\alpha-1}f_1(\alpha) \quad , \tag{10}$$

which differs only by a factor of 2 from the result of CT.

Result (9) can be interpreted that in the present model the correlation length in the REHAC with distribution (7) is proportional to $\beta^{\alpha-1}$, whereas the uniform chain has a (somewhat unphysical) exponential dependence on temperature of the correlation length. Although the result for the uniform chain should not be taken too seriously, the dramatic difference between the uniform chain and the REHAC demonstrates the substantial disorder in the REHAC.

In a magnetic field the Z_1 approximant to the partition function cannot be calculated exactly, because the eigenfunctions of the transfer matrix $\underline{T}_i^+$ are not orthogonal. In the low-temperature limit, however, this nonorthogonality is very small and will be neglected. In that case expression (8) for the transverse correlations remains valid, although the eigenvalues depend on the magnetic field, of course.

In the interesting intermediate-field region, $1\ll\beta h\ll J_0$ the result to leading order in (h/J_0) for the transverse correlations is given by

$$\langle S_{i,x}S_{i+j,x}\rangle=\tfrac{1}{4}[-1+4^{\alpha-1}(J_0/h)^{\alpha-1}]^{|j|} \quad . \tag{11}$$

The invariant parts of the longitudinal correlations are identical to the transverse correlations in the intermediate-field limit

$$\langle S_{i,z}S_{i+j,z}\rangle - \langle S_z\rangle^2 = \tfrac{1}{4}[-1+4^{\alpha-1}(J_0/h)^{\alpha-1}]^{|j|} \ . \tag{12}$$

Our results on the correlations can be summarized as follows. All the correlations decay exponentially with distance. The randomness of the model introduces in the zero-field limit, $h=0$ and $\beta J_0 \geqslant 1$, a correlation length proportional to $(\beta)^{\alpha-1}$, in the intermediate-field limit, $1 \leqslant \beta h \leqslant \beta J_0$, a correlation length proportional to $h^{1-\alpha}$. Interesting in this respect is the fact that an approximate calculation of a classical model gave the same dependence on β in the zero-field case.[4] This substantiates our earlier statement that the configurational averaging is obscuring underlying details, since in both models results for the unifrom chain differ dramatically.

The simplest possible way of relating dynamic correlations to static properties is the use of moments of the dynamic correlations.[10] At low temperatures this method usually works very reasonably, but fails completely for the high-temperature dynamics of low-dimensional systems.[11] We will apply it to the REHAC. We find that the second moment of $\langle S_{i,x}(0)S_{i+1,x}(t)\rangle$ in the rotating frame is given by

$$\begin{aligned} M_2 = & -2\langle J_i\rangle(\langle J_{i-1}S_{i-1,z}S_{i+1,z}\rangle + \langle J_{i-1}S_{i-1,y}S_{i+1,y}\rangle) \\ & +16\langle J_i^2 S_{i,x}S_{i+1,x}\rangle - 4\langle J_i^2\rangle \ . \end{aligned} \tag{13}$$

In the intermediate-field limit the result for M_2 is rather complicated, and we will discuss the salient features of the result. In the simplest possible description of the dynamics of proton spin-lattice relaxation, the relaxation rate is proportional to $M_2^{-1/2}$,[10] and in analyzing our result for M_2 we find that this would generate terms proportional to $h^{1-\alpha}$, $h^{2-\alpha}$, $h^{3-\alpha}$, and $h^{3-2\alpha}$ for the relaxation rate. The absence of any temperature dependence to leading order is rather disappointing. The strong temperature dependence found for the proton spin-lattice rate[2] for quinolinium$(TCNQ)_2$ shows probably that the method of moments is not suitable to treat the long-wavelength dynamics of the REHAC. This also means that short-chain calculations would not be able to explain the exchange-narrowing process.

It is also possible to use different distribution functions for the exchange constants. Soos and Bondeson[6] argue that fitting of experimental data on the magnetic susceptibility using a theory based on distribution (7) would lead to an extremely large and unphysical value for the exchange cutoff. This argument is not fair, because it was stated in all works that the cutoff is only of mathematical importance. Any microscopic calculation will show an increased probability for distances of the order of the nearest-neighbor distance. As a matter of fact the microscopic calculations of Theodorou and Cohen[4] demonstrate this in a nice way. In our model it is very simple to add a δ function to the distribution $P(J)$ centered at a typical nearest-neighbor value for J. This would not change the low-temperature results in any way, but would become important at higher temperatures, and would free the theory from unphysical cutoffs. The phenomenologic distribution introduced by Soos and Bondeson[6] consists of the sum of two δ functions of which the smallest is of the order of 60 K. Our model, which is not very suitable to treat this kind of very weakly disordered systems, nevertheless indicates that there would be substantial short-range order in this system for $T \ll 60$ K. This is also to be expected on general grounds. It is difficult to understand why such a system would not order three dimensionally at extremely low temperatures. Furthermore we think that it should be pointed out how a microscopic derivation can be given for an independent bond-disorder distribution starting from a site-distribution problem.

We have presented a simple quantum-mechanical model for $S=\frac{1}{2}$ REHAC. Without destroying the symmetry of the model, the zero-magnetic-field thermodynamic properties could be shown to be equivalent to the exchange-coupled pair model.[5] Correlations were shown to decay exponentially with distance in this model. A calculation of the second moment of a dynamic two-spin correlation function was performed. No meaningful results were obtained when we tried to extract the correlation time of this correlation function from its second moment.

The path-summation representation we used was first introduced by Suzuki *et al.*[8] This method is in principle very powerful because it allows the use of Monte Carlo methods for quantum-statistical mechanics.[12] We have tried this approach also here, but ran into as yet not soluble numerical problems associated with distribution (7). In the path-summation method one works with exponential operators, and coupling constants generated with probability (7) lead to a dynamic range of these operators which goes beyond the range of even the most powerful computer.

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